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Three-dimensional distributions of oxygen in graphite and metal tube atomizers for analytical atomic spectrometry

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Abstract

A mathematical model that allows the calculation of the steady-state three-dimensional distributions of oxygen molecules inside both graphite and metal (tantalum and tungsten) tube atomizers is developed. The model takes into account the ingress of oxygen through the sample dosing hole and through the tube ends and the kinetics of the heterogeneous oxidation reactions at the atomizer walls. Imaged representations of the calculated three-dimensional distributions of molecular oxygen in both graphite furnaces and metal tube atomizers are given. The results obtained for pyrolytic graphite coated graphite furnaces showed that the oxygen concentration is much higher and the distribution of the concentration much more uniform, than is generally accepted. In contrast to the distributions of oxygen calculated for graphite furnaces, those in metal tubes are strongly non-uniform and, when the ingress of oxygen through both the sample dosing hole and through the tube ends is accounted for, the molecular cloud consists of three independent structures. These structures are confined to the ends and the centre of the tube. An expression that allows the estimation of the total number, Nt, of oxygen molecules within a tube atomizer resulting from their ingress at a rate of J (molecules s -1) through the sample dosing hole is obtained: Nt=JR/ [2k(T)], where R is the radius of the tube and k(T) is the temperature dependent rate constant for heterogeneous reactions with the tube wall. Using this equation an estimation of the oxygen partial pressure within a Perkin-Elmer HGA-type graphite furnace of ≈5×10-5 atm (1 atm=1.013×105 Pa) at T=2100 K was obtained. It is shown that, under typical operating conditions for Perkin-Elmer HGA-type atomizers, J≈ 1014-1016 molecules s-1. A protection coefficient to the ingress of oxygen through the sample dosing hole is introduced and it is shown that the flow of the external Ar purge gas reduces the diffusional ingress of oxygen by a factor of 102-103. The steady-state results reported above are also applicable to non-stationary conditions if the heating rate of the atomizer does not exceed a certain value (quasi-stationary condition). The criteria for establishing these quasi-stationary conditions are proposed.

Keywords

Electrothermal atomic absorption spectrometry, Graphite furnace, Metal furnace, Three-dimensional distribution of oxygen